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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C10G 11/04, 11/05, C07C 4/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 96/34930</b> <b>(43) International Publication Date:</b> 7 November 1996 (07.11.96)
<b>(21) International Application Number:</b> PCT/US96/05253 <b>(22) International Filing Date:</b> 15 April 1996 (15.04.96)  <b>(30) Priority Data:</b> 08/435,765      5 May 1995 (05.05.95)      US  <b>(71) Applicant:</b> MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).  <b>(72) Inventors:</b> CHESTER, Arthur, Warren; 517 Country Club Drive, Cherry Hill, NJ 08003 (US). KRESGE, Charles, Theodore; 600 Thomcroft Drive, West Chester, PA 19380 (US). QUINONES, Augusto, Rodolfo; Apartment 1002, One Signature Pt. Drive, League City, TX 77573 (US). VALYOCSIK, Ernest, W.; 960 Randolph Drive, Lower Makefield Turnpike, Yardley, PA 19067 (US).  <b>(74) Agents:</b> SANTINI, Dennis, P. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).		<b>(81) Designated States:</b> AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CATALYTIC CONVERSION WITH MCM-58  <b>(57) Abstract</b>  A process is provided for converting feedstock hydrocarbon compounds to product hydrocarbon compounds having a lower molecular weight than feedstock hydrocarbon compounds over a catalyst composition which comprises MCM-58 or a mixture of MCM-58 and another, e.g., intermediate- or large-pore, molecular sieve component. An embodiment of the present invention comprises an improved catalytic cracking process to produce high octane gasoline and lower molecular weight olefins, e.g. propylene.		

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## CATALYTIC CONVERSION WITH MCM-58

The present invention relates to a process for converting, e.g., cracking, a hydrocarbon feed over a particular catalyst composition to produce conversion product hydrocarbon compounds of lower molecular weight than feed hydrocarbons, e.g., product comprising a high octane gasoline fraction and increased lower olefins, especially propylene and butylene. The catalyst composition for use herein comprises synthetic porous crystalline MCM-58.

Catalytic cracking operations are commercially employed in the petroleum refining industry to produce useful products, such as high quality gasoline and fuel oils, from hydrocarbon-containing feeds. The endothermic catalytic cracking of hydrocarbons is most commonly practiced in accordance with two known catalytic cracking operations, namely, fluid catalytic cracking (FCC) and moving bed catalytic cracking.

Generally, both fluid catalytic cracking and moving bed operations are commercially practiced in a cyclic mode. During these operations, the hydrocarbon feedstock is contacted with hot, active, solid particulate catalyst without added hydrogen, for example, at pressures of up to about 50 psig and temperatures up to about 650°C. As the hydrocarbon feed is cracked in the presence of cracking catalyst to form more valuable and desirable products, undesirable carbonaceous residue known as "coke" is deposited on the catalyst. The spent catalyst contains coke as well as metals that are present in the feedstock.

In FCC operations, the catalyst is a fine powder with particle sizes of about 20-200 microns in diameter and with an average size of approximately 60-100 microns. The fine powder is propelled upwardly through a riser reaction zone, fluidized and thoroughly mixed with the hydrocarbon feed. The hydrocarbon feed is cracked at high temperatures by the catalyst and separated into various hydrocarbon products.

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The coked catalyst particles are separated from the cracked hydrocarbon products, and after stripping, are transferred into a regenerator where the coke is burnt off to regenerate the catalyst. The regenerated catalyst then flows downwardly from the regenerator to the base of the riser.

The cycles of cracking and regeneration at high flow rates and temperatures have a tendency to physically break down the catalyst into smaller particles, called "fines" which have a diameter of up to 20 microns as compared to the average diameter of the catalyst particle of about 60 to about 100 microns. In determining the unit retention of catalysts, and accordingly their cost efficiency, attrition resistance is a key parameter. While the initial size of the particles can be controlled relatively easily by controlling the initial spray drying of the catalyst, if the attrition resistance is poor, the catalytic cracking unit may produce a large amount of the 0 - 20 micron fines which should not be released into the atmosphere.

Commercial catalytic cracking units include cyclones and electrostatic precipitators to prevent fines from becoming airborne. Those skilled in the art appreciate that excessive generation of catalyst fines increases the cost of catalyst to the refiner.

Additionally, the catalyst particles cannot be too large in diameter, or the particles may not be sufficiently fluidized. Therefore, the catalysts are preferably maintained under 120 to 150 microns in diameter.

Another consideration is deposition of coke on the catalyst particles which is generally considered undesirable for two reasons: first, it inevitably results in a decline in catalytic activity to a point where the catalyst is considered to have become "spent"; and second, coke generally forms on the catalyst at the expense of more desired light liquid products. To regenerate the catalytic activity, the hydrocarbon residues of the coke must be

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burnt off the "spent" catalyst at elevated temperatures in a regenerator.

Current worldwide refinery trends indicate a continuing need to process heavier feed stock. As a result, many refineries will be processing feedstock containing resids or deeper cut gas oils which have high metals contents. The enhancement of octane produced in catalytic cracking operations is an important goal in the preparation of zeolite containing catalysts. The environmental regulations in the United States and abroad, and the phaseout of lead additives for gasolines in both the U.S. and abroad, provide a strong incentive for refineries to use catalysts which produce increased octane gasolines from heavier metals contaminated feedstock.

Therefore, it would be highly desirable to have a catalyst with high attrition resistance. It would also be desirable to provide fluid catalysts having reduced manufacturing costs and improved catalytic activity for octane enhancement. Those skilled in the art will appreciate that improved attrition resistance as well as improved activity will translate into reduced catalyst makeup rates.

U.S. Patent 5,110,776 teaches a method for preparing FCC catalyst comprising modifying the zeolite, e.g., ZSM-5, with phosphorus. U.S. Patent 5,126,298 teaches manufacture of an FCC catalyst comprising zeolite, e.g., ZSM-5, clay, and phosphorus. Phosphorus treatment has been used on faujasite-based cracking catalysts for metals passivation (see U.S. Patents 4,970,183 and 4,430,199); reducing coke make (see U.S. Patents 4,567,152; 4,584,091; and 5,082,815); increasing activity (see U.S. Patents 4,454,241 and 4,498,975); increasing gasoline selectivity (See U.S. Patent 4,970,183); and increasing steam stability (see U.S. Patents 4,765,884 and 4,873,211).

In U.S. Patent 3,758,403, use of large-pore cracking catalyst with large amounts of ZSM-5 additive gives only modest increase in light olefin production. A 100 %

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increase in ZSM-5 content (from 5 wt.% ZSM-5 to 10 wt.% ZSM-5) increased the propylene yield less than 20 %, and decreased slightly the potential gasoline yield (C<sub>5</sub>+ gasoline plus alkylate).

5 U.S. Patent 4,309,280 teaches adding very small amounts of powdered, neat ZSM-5 catalyst, characterized by a particle size below 5 microns. Adding as little as 0.25 wt.% ZSM-5 powder to the FCC catalyst inventory increased LPG production 50%. Small amounts of neat powder behaved  
10 much like larger amounts of ZSM-5 disposed in larger particles.

A way to add a modest amount of ZSM-5 to an FCC unit is disclosed in U.S. Patent 4,994,424. ZSM-5 additive is added to the equilibrium catalyst in a programmed manner so  
15 an immediate boost in octane number, typically 1/2-2 octane number, is achieved.

U.S. Patent 4,927,523 teaches a way to add large amounts of ZSM-5 to a unit without exceeding wet gas compressor limits. Large amounts are added and cracking  
20 severity is reduced in the FCC unit for several days.

It is an object of the present invention to provide an improved cracking process using an improved catalyst composition.

It is also an object of the present invention to  
25 provide an improved process using an improved catalyst composition to enhance production of valuable light olefins, e.g., propylene and butylene.

These and other objects are achieved by the present invention which provides a process for converting feedstock  
30 hydrocarbon compounds to product hydrocarbon compounds of lower molecular weight than the feedstock hydrocarbon compounds. The process comprises contacting the feedstock at conversion conditions with an improved catalyst composition comprising a novel porous crystalline  
35 composition of matter, named MCM-58.

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More particularly, the invention provides a hydrocarbon cracking process which uses the improved catalyst composition comprising MCM-58.

In catalytic cracking, high molecular weight hydrocarbons are converted to lower molecular weight hydrocarbons of suitable volatility to permit their use as liquid fuels. The combustion characteristics of gasoline are assessed empirically by assigning the fuel an octane rating. This is generally defined as a comparison with a primary reference which is the percentage of iso-octane (2,2,4-trimethylpentane) in an n-heptane/iso-octane mixture to which the gasoline under examination is equivalent in terms of combustion behavior when considering the octane ratings of n-heptane and iso-octane to be zero and 100 respectively. Both RON and MON can be tested on the same single-cylinder, four-stroke engine of standardized design. RON signifies the research octane number, MON signifies the motor octane number, and the terms are used to describe the knocking characteristics of gasoline, that is, its combustion behavior. For a measurement of RON, the engine speed used is 600 rpm which yields results comparable to an automobile engine operated at low speed. For a measurement of MON, the engine speed is 900 rpm which approximates higher speed cruising conditions. Generally, higher octane numbers are found by the research method compared to the motor method for the same gasoline sample. The average of the RON and MON, known as the road octane number, gives an indication of typical performance in an engine. The higher the octane, the better the combustion behavior in a spark-ignition engine. It has been found that road octane number correlates much more closely to the motor octane number than the research octane. Generally, aromatics and branched paraffinic and olefinic hydrocarbons have higher octane values than acyclic or linear paraffinic hydrocarbons.

In conjunction with catalytic cracking to produce gasoline product, alkylate and potential alkylate may



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result from the cracking process. This indirectly leads to product of increased octane because high octane, highly branched paraffinic gasoline blending stocks are produced principally by alkylation of  $C_3$  and  $C_4$  olefins with isobutane. Unlike cracking, alkylation makes larger branched hydrocarbons from smaller hydrocarbons and these larger branched hydrocarbons are inherently higher in octane.

The present process provides not only a high octane product, but significantly more light olefins, especially propylene and/or butylene. The lower olefins of this product are high quality, petrochemical grade, and may be used for manufacture of valuable ethers and/or alcohols, or as alkylating agents.

#### Feeds

The feedstock, that is, the hydrocarbons to be cracked, may include in whole or in part, a gas oil (e.g., light, medium, or heavy gas oil) having an initial boiling point above about  $204^{\circ}\text{C}$ , a 50 % point of at least about  $260^{\circ}\text{C}$ , and an end point of at least about  $315^{\circ}\text{C}$ . The feedstock may also include deep cut gas oil, vacuum gas oil, thermal oil, residual oil, cycle stock, whole top crude, tar sand oil, shale oil, synthetic fuel, heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tar, pitches, asphalts, hydrotreated feedstocks derived from any of the foregoing, and the like. As will be recognized, the distillation of higher boiling petroleum fractions above about  $400^{\circ}\text{C}$  must be carried out under vacuum in order to avoid thermal cracking. The boiling temperatures utilized herein are expressed in terms of convenience of the boiling point corrected to atmospheric pressure. Resids or deeper cut gas oils having an end point of up to about  $700^{\circ}\text{C}$ , even with high metals contents, can also be cracked using the invention.

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Process

The present invention provides a process for converting feedstock hydrocarbon compounds to product hydrocarbon compounds of lower molecular weight than the feedstock hydrocarbon compounds. In particular, the present invention provides a process for catalytically cracking a hydrocarbon feed to a mixture of products comprising gasoline, alkylate, potential alkylate, and lower olefins, e.g. propylene, in the presence of a cracking catalyst under catalytic cracking conditions. Catalytic cracking units which are amenable to the process of the invention operate at temperatures from about 400°C to about 650°C, usually from about 450°C to about 600°C, and under reduced, atmospheric, or superatmospheric pressure, usually from about atmospheric to about 5 atmospheres. The catalytic process can be either fixed bed, moving bed, transfer line, or fluidized bed, and the hydrocarbon flow may be either concurrent or countercurrent to the catalyst flow. The process of the invention is particularly applicable to the Fluid Catalytic Cracking (FCC) or Thermoform Catalytic Cracking (TCC) processes. In both of these processes, the hydrocarbon feed and catalyst are passed through a reactor and the catalyst is regenerated. The two processes differ substantially in the size of the catalyst particles and in the engineering contact and transfer which is at least partially a function of catalyst size.

The TCC process is a moving bed and the catalyst is in the shape of pellets or beads having an average particle size of about one-sixty-fourth to one-fourth inch. Active, hot catalyst beads progress downwardly cocurrent with a hydrocarbon charge stock through a cracking reaction zone. The hydrocarbon products are separated from the coked catalyst and recovered, and the catalyst is recovered at the lower end of the zone and regenerated.

Typically preferred TCC conversion conditions include an average reactor temperature of from about 450°C to about

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540°C; catalyst/oil volume ratio of from about 2 to about 7; reactor volume hourly space velocity of from about 1 to about 5 vol./hr./vol.; and recycle to fresh feed ratio of from 0 to about 0.5 (volume).

5       The process of the invention is particularly applicable to Fluid Catalytic Cracking. In fluidized catalytic cracking processes, the catalyst is a fine powder of about 10 to 200 microns. This powder is generally suspended in the feed and propelled upward in a reaction  
10       zone. A relatively heavy hydrocarbon feedstock, e.g., a gas oil, is admixed with a suitable cracking catalyst to provide a fluidized suspension and cracked in an elongated reactor, or riser, at elevated temperatures to provide a mixture of lighter hydrocarbon products. The gaseous  
15       reaction products and spent catalyst are discharged from the riser into a separator, e.g., a cyclone unit, located within the upper section of an enclosed stripping vessel, or stripper, with the reaction products being conveyed to a product recovery zone and the spent catalyst entering a  
20       dense catalyst bed within the lower section of the stripper. In order to remove entrained hydrocarbons from the spent catalyst prior to conveying the latter to a catalyst regenerator unit, an inert stripping gas, e.g., steam, is passed through the catalyst bed where it desorbs  
25       such hydrocarbons conveying them to the product recovery zone. The fluidizable catalyst is continuously circulated between the riser and the regenerator and serves to transfer heat from the latter to the former thereby supplying the thermal needs of the cracking reaction which  
30       is endothermic.

      Gas from the FCC main-column overhead receiver is compressed and directed with primary-absorber bottoms and stripper overhead gas through a cooler to the high pressure receiver. Gas from this receiver is routed to the primary  
35       absorber, where it is contacted by the unstabilized gasoline from the main-column overhead receiver. The net effect of this contacting is a separation between C<sub>3</sub>+ and

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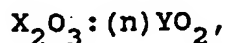
C<sub>2</sub>- fractions in the feed to the primary absorber. Primary absorber off-gas is directed to a secondary or sponge absorber, where a circulating stream of light cycle oil from the main column is used to absorb most of the remaining C<sub>5</sub>+ material in the sponge absorber feed. Some C<sub>3</sub> and C<sub>4</sub> materials are also absorbed. The sponge-absorber rich oil is returned to the FCC main column. The sponge-absorber overhead, with most of the valuable C<sub>4</sub>+ material removed but including H<sub>2</sub>S, is sent to the fuel gas or other process streams.

Liquid from the high pressure separator is sent to a stripper where most of the C<sub>2</sub>- is removed overhead and sent back to the high pressure separator. The bottoms liquid from the stripper is sent to the debutanizer, where an olefinic C<sub>3</sub>-C<sub>4</sub> product is further separated for gasoline production. The debutanizer bottoms, that is, the stabilized gasoline, is sent to treating, if necessary, and then to storage. The C<sub>3</sub> and C<sub>4</sub> product olefins can be directed to an alkylation unit to produce a high octane gasoline by the reaction of an iso-paraffin (usually isobutane) with one or more of the low molecular weight olefins (usually propylene and butylene).

The FCC conversion conditions include a riser top temperature of from about 500°C to about 595°C, preferably from about 520°C to about 565°C, and most preferably from about 530°C to about 550°C; catalyst/oil weight ratio of from about 3 to about 12, preferably from about 4 to about 11, and most preferably from about 5 to about 10; and catalyst residence time of from about 0.5 to about 15 seconds, preferably from about 1 to about 10 seconds.

#### Catalyst

The crystalline MCM-58 material for use herein as catalyst component has a composition comprising the molar relationship:



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wherein X is a trivalent element, such as aluminum, boron, iron, indium, and/or gallium, preferably aluminum; Y is a tetravalent element such as silicon, tin, and/or germanium, preferably silicon; and n is from greater than about 10 to about 1000, usually from greater than about 10 to about 400, more usually from about 20 to about 200. In the as-synthesized form, the material has a formula, on an anhydrous basis and in terms of moles of oxides per n moles of  $YO_2$ , as follows:

10  $(0.1-2)M_2O:(0.2-2)R:X_2O_3:nYO_2$   
wherein M is an alkali or alkaline earth metal, and R is an organic moiety. The M and R components are associated with the material as a result of their presence during crystallization, and are easily removed by post-  
15 crystallization methods hereinafter more particularly described.

The MCM-58 for use in the invention is thermally stable and in the calcined form exhibits significant hydrocarbon sorption capacity. To the extent desired, the  
20 original sodium and/or potassium cations of the as-synthesized material can be replaced in accordance with techniques well known in the art, at least in part, by ion exchange with other cations. Preferred replacing cations include metal ions, hydrogen ions, hydrogen precursor,  
25 e.g., ammonium, ions and mixtures thereof. Particularly preferred cations are those which tailor the catalytic activity for certain hydrocarbon conversion reactions. These include hydrogen, rare earth metals and metals of Groups IIA, IIIA, IVA, IB, IIB, IIIB, IVB and VIII of the  
30 Periodic Table of the Elements.

In the as-synthesized form, the crystalline MCM-58 material for use in the invention appears to be a single crystalline phase. It can be prepared in essentially pure form with little or no detectable impurity crystal phases  
35 and has an X-ray diffraction pattern which is distinguished from the patterns of other known as-synthesized or

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thermally treated crystalline materials by the lines listed in Table I below:

TABLE I

	<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, I/I<sub>0</sub> x 100</u>
5		
	10.89 ± 0.30	S-VS
10	9.19 ± 0.30	VW
	6.55 ± 0.29	VW-W
	5.86 ± 0.28	VW-W
	5.57 ± 0.27	VW-W
	5.43 ± 0.26	VW-W
15	4.68 ± 0.25	VW-m
	4.36 ± 0.25	W-VS
	4.17 ± 0.23	VW-m
	4.12 ± 0.23	VW-S
	3.78 ± 0.20	WV-S
20	3.61 ± 0.15	VW-W
	3.54 ± 0.15	VW
	3.44 ± 0.15	VW-m
	3.37 ± 0.15	VW-m
	3.06 ± 0.15	VW-W
25	2.84 ± 0.15	VW
	2.72 ± 0.13	VW
	2.66 ± 0.12	VW
	2.46 ± 0.12	VW
30	2.17 ± 0.10	VW

These X-ray diffraction data were collected with a Scintag diffraction system, equipped with a germanium solid state detector, using copper K-alpha radiation. The diffraction data were recorded by step-scanning at 0.02 degrees of two-theta, where theta is the Bragg angle, and a counting time of 10 seconds for each step. The interplanar spacings, d's, were calculated in Angstrom units (A), and the relative intensities of the lines, I/I<sub>0</sub> is one-hundredth of the intensity of the strongest line, above background, were derived with the use of a profile fitting routine (or second derivative algorithm). The intensities are uncorrected for Lorentz and polarization effects. The relative intensities are given in terms of the symbols vs = very strong (80-100), s = strong (60-80), m = medium (40-60), w = weak (20-40), and vw = very weak (0-20). It should be understood that

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diffraction data listed for this sample as single lines may consist of multiple overlapping lines which under certain conditions, such as differences in crystallographic changes, may appear as resolved or partially resolved lines. Typically, crystallographic changes can include minor changes in unit cell parameters and/or a change in crystal symmetry, without a change in the structure. These minor effects, including changes in relative intensities, can also occur as a result of differences in cation content, framework composition, nature and degree of pore filling, and thermal and/or hydrothermal history.

When used as a catalyst, the MCM-58 may be subjected to treatment to remove part or all of any organic constituent. The crystalline material can also be used as a catalyst in intimate combination with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such component can be in the composition by way of cocrystallization, exchanged into the composition to the extent a Group IIIA element, e.g., aluminum, is in the structure, impregnated therein or intimately physically admixed therewith. Such component can be impregnated in or on to it such as, for example, by, in the case of platinum, treating the silicate with a solution containing a platinum metal-containing ion. Thus, suitable platinum compounds for this purpose include chloroplatinic acid, platinumous chloride and various compounds containing the platinum amine complex.

The crystalline MCM-58 material can be transformed by thermal treatment. This thermal treatment is generally performed by heating at a temperature of at least about 370°C for at least 1 minute and generally not longer than 20 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. The thermal treatment can be

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performed at a temperature up to about 925°C. The thermally treated product, especially in its metal, hydrogen and ammonium forms, is particularly useful in the catalysis of certain organic, e.g., hydrocarbon, conversion reactions.

As a catalyst component in the present conversion process, MCM-58 should be dehydrated, at least partially. This can be done by heating to a temperature in the range of 200°C to about 370°C in an atmosphere such as air, nitrogen, etc., and at atmospheric, subatmospheric or superatmospheric pressures for between 30 minutes and 48 hours. Dehydration can also be performed at room temperature merely by placing the MCM-58 in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

MCM-58 can be prepared from a reaction mixture containing sources of alkali or alkaline earth metal (M), e.g., sodium and/or potassium, cation, an oxide of trivalent element X, e.g., aluminum and/or boron, an oxide of tetravalent element Y, e.g., silicon, directing agent (R), and water, said reaction mixture having a composition, in terms of mole ratios of oxides, within the following ranges:

	<u>Reactants</u>	<u>Useful</u>	<u>Preferred</u>
25	$YO_2/X_2O_3$	15 to 1000	25 to 500
	$H_2O/YO_2$	5 to 200	20 to 100
	$OH^-/YO_2$	0 to 3	0.10 to 0.50
	$M/YO_2$	0 to 3	0.10 to 2
30	$R/YO_2$	0.02 to 1.0	0.10 to 0.50

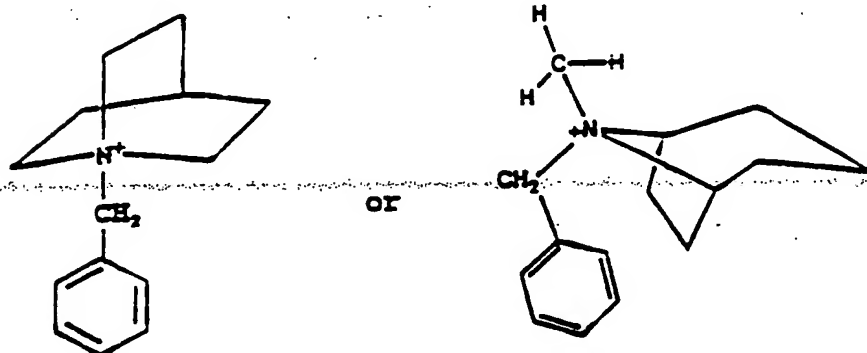
In this synthesis method, the preferred source of  $YO_2$  comprises predominately solid  $YO_2$ , for example at least about 30 wt.% solid  $YO_2$ . Where  $YO_2$  is silica, the use of a silica source containing at least about 30 wt.% solid silica, e.g., Ultrasil (a precipitated, spray dried silica containing about 90 wt.% silica) or HiSil (a precipitated



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hydrated  $\text{SiO}_2$  containing about 87 wt.% silica, about 6 wt.% free  $\text{H}_2\text{O}$  and about 4.5 wt.% bound  $\text{H}_2\text{O}$  of hydration and having a particle size of about 0.02 micron) is preferred for MCM-58 formation from the above mixture. Preferably, therefore, the  $\text{YO}_2$ , e.g., silica, source contains at least about 30 wt.% solid  $\text{YO}_2$ , e.g., silica, and more preferably at least about 40 wt.% solid  $\text{YO}_2$ , e.g., silica.

The organic directing agent R for use herein above is either the cation benzylquinuclidinium, having a formula  $\text{C}_{14}\text{H}_{20}\text{N}^+$  or the cation benzyltropanium, having a formula  $\text{C}_{15}\text{H}_{22}\text{N}^+$ , and may be represented as follows:



The sources of these organic cations may be, for example, the halide, e.g., chloride or bromide, or hydroxide salt. The source of organic directing agents used in the following examples was synthesized as follows:

(1) Benzylquinuclidinium halide, i.e., bromide, was synthesized by reacting benzylbromide and quinuclidine in absolute ethanol solvent in a flask equipped with a reflux condenser, a thermometer and a stirrer. The flask was charged with 60.0 grams of benzylbromide with 200 ml of absolute ethanol. Then 33.4 grams of quinuclidine dissolved in 300 ml of absolute ethanol was transferred to the flask. Heating and stirring of the flask reaction mixture commenced immediately.

The reaction mixture was refluxed ( $\sim 70^\circ\text{C}$ ) overnight with stirring before quenching the reaction vessel in a dry ice-acetone bath to  $-40^\circ\text{C}$ . The cold crystalline product

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was separated from the solvent, filtered, and washed with anhydrous diethylether on a Büchner funnel. The crystals were dried in an air stream, then chemically analyzed. The benzylquinuclidium bromide product of this example was  
5 found to be composed of 56.13 wt.% C, 7.46 wt.% H, 4.66 wt.% N and 28.13 wt.% Br;

(2) Benzyltropanium halide, i.e., bromide, was synthesized by reacting benzylbromide and tropane in absolute ethanol solvent in a flask equipped with a reflux  
10 condenser, a thermometer and a stirrer. The flask was charged with 60.0 grams of benzylbromide with 300 ml of absolute ethanol. Then 37.6 grams of tropane dissolved in 300 ml of absolute ethanol was transferred to the flask. Heating and stirring of the flask reaction mixture  
15 commenced immediately.

The reaction mixture was refluxed (~70°C) overnight with stirring before quenching the reaction vessel in a dry ice-acetone bath to -40°C. The cold crystalline product was separated from the solvent, filtered, and washed with  
20 anhydrous diethylether on a Büchner funnel. The benzyltropanium bromide product crystals were then dried in an air stream.

Crystallization of the MCM-58 can be carried out at either static or stirred conditions in a suitable reactor  
25 vessel, such as for example, polypropylene jars or teflon lined or stainless steel autoclaves. The total useful range of temperatures for crystallization is from about 80°C to about 250°C for a time sufficient for crystallization to occur at the temperature used, e.g.,  
30 from about 12 hours to about 100 days. Thereafter, the crystals are separated from the liquid and recovered.

It should be realized that the reaction mixture components can be supplied by more than one source. The reaction mixture can be prepared either batchwise or  
35 continuously. Crystal size and crystallization time of the new crystalline material will vary with the nature of the

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reaction mixture employed and the crystallization conditions.

5        Synthesis of MCM-58 crystals may be facilitated by the presence of at least 0.01 percent, preferably 0.10 percent and still more preferably 1 percent, seed crystals (based on total weight) of crystalline product.

10        The MCM-58 crystals can be shaped into a wide variety of particle sizes for use herein. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as an extrudate having particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the crystals can be extruded before drying or partially dried and then  
15        extruded.

      The catalyst composition for use herein will comprise  
20        (1) MCM-58 alone as the active component, or (2) a mixture of MCM-58 with another zeolite molecular sieve, or (3) the MCM-58 may be used as an additive catalyst to a large-pore molecular sieve catalyst composition found in cracking catalyst inventory.

      The other zeolite component of catalyst composition  
25        (2) above may be a large-pore crystalline material having pore openings of greater than about 7 Angstroms diameter such as, for example, zeolite X (U.S. Patent 2,882,442); REX; zeolite Y (U.S. Patent 3,130,007); Ultrastable Y (USY) (U.S. Patent 3,449,070); Rare Earth exchanged Y (REY) (U.S. Patent 4,415,438); Rare Earth exchanged USY (REUSY); Dealuminated Y (DeAl Y) (U.S. Patents 3,442,792 and  
30        4,331,694); Ultrahydrophobic Y (UHPY) (U.S. Patent 4,401,556); and/or dealuminated silicon-enriched zeolites, e.g., LZ-210 (U.S. Patent 4,678,765); ZSM-20 (U.S. Patent 3,972,983); Beta (U.S. Patent 3,308,069); L (U.S. Patents 3,216,789 and 4,701,315); silicoaluminophosphates SAPO-5;  
35        SAPO-37; SAPO-40; MCM-9; metalloaluminophosphate MAPO-36; aluminophosphate VPI-5; or mesoporous crystalline material MCM-41; or an intermediate pore crystalline material having

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pore openings of from about 4 Angstroms to about 7 Angstroms diameter such as, for example, zeolites ZSM-5; ZSM-11; ZSM-22; ZSM-23; ZSM-35; ZSM-48; ZSM-57; or silicoaluminophosphate SAPO-31; or small pore zeolite having pore openings of less than about 4 Angstroms diameter including, for example, erionite and ZSM-34. This other zeolite component may be a mixture of large-pore, intermediate-pore, and/or small-pore crystalline materials. A non-limiting example of this includes the combination of zeolite having the structure of ZSM-5 having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio of greater than about 20/1, e.g., about 55/1, and zeolite selected from the group consisting of USY, REY, and REUSY.

The large-pore molecular sieves for use herein when combined with MCM-58 or to which is added MCM-58 as an additive catalyst, i.e., catalyst composition (3) above, may comprise any active component which has cracking activity and which has a pore opening of greater than about 7 Angstroms in effective diameter. The active component may be a conventional large-pore molecular sieve including zeolite X; REX; zeolite Y; Ultrastable Y (USY); Rare Earth exchanged Y (REY); Rare Earth exchanged USY (REUSY); Dealuminated Y (DeAl Y); Ultrahydrophobic Y (UHPY); and/or dealuminated silicon-enriched zeolites, e.g., LZ-210. Preferred are higher silica forms of zeolite Y. ZSM-20; zeolite Beta; zeolite L; and naturally occurring zeolites such as faujasite, mordenite and the like may also be used. These materials may be subjected to conventional treatments, such as impregnation or ion exchange with rare earths to increase stability. In current commercial practice most cracking catalysts contain these large-pore molecular sieves. The preferred molecular sieve of those listed above is a zeolite Y, more preferably an REY, USY or REUSY.

Other large-pore crystalline molecular sieves include pillared silicates and/or clays; aluminophosphates, e.g.,  $\text{ALPO}_4$ -5,  $\text{ALPO}_4$ -8, VPI-5; silicoaluminophosphates, e.g.,

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SAPO-5, SAPO-37, SAPO-40, MCM-9; and other metal aluminophosphates. Mesoporous crystalline material for use as the molecular sieve includes MCM-41. These are variously described in U.S. Patents 4,310,440; 4,440,871; 4,554,143; 5 4,567,029; 4,666,875; 4,742,033; 4,880,611; 4,859,314; 4,791,083; 5,102,643; and 5,098,684, each incorporated herein by reference.

The preparation of some molecular sieve-containing catalysts may require reduction of the sodium content, as well as conversion to the acid (protonated) form. For 10 example, with zeolites this can be accomplished by employing the procedure of converting the zeolite to an intermediate ammonium form as a result of ammonium ion exchange followed by calcination to provide the hydrogen 15 form. The operational requirements of these procedures are well known in the art.

The source of the ammonium ion is not critical; thus the source can be ammonium hydroxide or an ammonium salt such as ammonium nitrate, ammonium sulfate, ammonium 20 chloride and mixtures thereof. These reagents are usually in aqueous solutions. By way of illustration, aqueous solutions of 1N  $\text{NH}_4\text{OH}$ , 1N  $\text{NH}_4\text{NO}_3$ , 1N  $\text{NH}_4\text{Cl}$ , and 1N  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$  have been used to effect ammonium ion exchange. The pH of the ion exchange is not critical but is generally 25 maintained at 7 to 12. Ammonium exchange may be conducted for a period of time ranging from about 0.5 to about 20 hours at a temperature ranging from ambient up to about 100°C. The ion exchange may be conducted in a single stage or in multiple stages. Calcination of the ammonium 30 exchanged zeolite will produce its acid form. Calcination can be effected at temperatures up to about 550°C.

The MCM-58, other zeolite molecular sieve, or large-pore molecular sieve catalyst component may include phosphorus or a phosphorus compound for any of the 35 functions generally attributed thereto, such as, for example, attrition resistance, stability, metals passivation, and coke make reduction.

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Suitable sources of phosphorus for use in preparing the catalyst composition and/or additive catalyst used in the present invention include phosphoric acid, ammonium dihydrogen phosphate, ammonium monohydrogen phosphate, triammonium phosphate, ammonium hypophosphate, ammonium orthophosphate, ammonium dihydrogen orthophosphate, ammonium monohydrogen orthophosphate, ammonium hypophosphite, ammonium dihydrogen orthophosphite, and mixtures thereof.

To prepare the other zeolite molecular sieve or the large-pore molecular sieve component for use herein, a slurry may be formed by deagglomerating the molecular sieve, preferably in an aqueous solution. A slurry of the matrix material may be formed by mixing the desired matrix components such as clay and/or inorganic oxide in an aqueous solution. The molecular sieve slurry and the matrix slurry are then well mixed and spray dried to form catalyst particles of, for example, less than 200 microns in diameter.

It is noted that additive catalyst with different properties is often used along with the conventional catalyst to form an optional mixed catalyst system. Commercially used additives are shape-selective zeolites. Zeolites having a Constraint Index of 1-12 can be used for this purpose. Details of the Constraint Index test are provided in J.Catalysis, 67, 218-222 (1981) and in U.S. Patent 4,711,710.

Conventional shape-selective zeolites useful for this purpose are exemplified by large-pore (e.g., greater than about 7 Angstroms pore size) zeolite Beta (U.S. Patent 3,308,069); intermediate pore (e.g., pore size of from about 4 to about 7 Angstroms) zeolites ZSM-5 (U.S. Patent 3,702,886 and Re. 29,948); ZSM-11 (U.S. Patent 3,709,979); ZSM-12 (U.S. Patent 4,832,449); ZSM-22 (U.S. Patent 4,556,477); ZSM-23 (U.S. Patent 4,076,842); ZSM-35 (U.S. Patent 4,016,245); ZSM-48 (U.S. Patent 4,397,827); ZSM-57 (U.S. Patent 4,046,685); PSH-3 (U.S. Patent 4,439,409); and

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MCM-22 (U.S. Patent 4,954,325); and small pore (e.g., having pore openings of less than about 4 Angstroms diameter) zeolites ZSM-34 and erionite, either alone or in combination. In addition, the catalyst composition may include metals useful in promoting the oxidation of carbon monoxide to carbon dioxide under regenerator conditions as described in U.S. Patent 4,350,614. The additive catalyst may also include phosphorus or a phosphorus compound for any of the functions generally attributed thereto.

The matrix, i.e., binder, materials used for the catalyst composition are resistant to the temperatures and other conditions e.g., mechanical attrition, which occur in various hydrocarbon conversion processes such as cracking. It is generally necessary that the catalysts be resistant to mechanical attrition, that is, the formation of fines which are small particles, e.g., less than 20  $\mu\text{m}$ . The cycles of cracking and regeneration at high flow rates and temperatures, such as in an FCC process, have a tendency to break down the catalyst into fines, as compared with an average diameter of catalyst particles of about 60-100 microns. In an FCC process, catalyst particles range from about 20 to about 200 microns, preferably from about 20 to 120 microns. Excessive generation of catalyst fines increases the refiner's catalyst costs.

The matrix may fulfill both physical and catalytic functions. Matrix materials include active or inactive inorganic materials such as clays, and/or metal oxides such as alumina or silica, titania, zirconia, or magnesia. The metal oxides may be in the form of a gelatinous precipitate or gel.

Use of an active matrix material in conjunction with the molecular sieve component that is combined therewith, may enhance the conversion and/or selectivity of the overall catalyst composition in certain hydrocarbon conversion processes. Inactive materials may serve as diluents to control the amount of conversion in a given process so that products can be obtained economically and

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in an orderly fashion without employing other means for controlling the rate of reaction. These materials may be incorporated as naturally occurring clays to improve the attrition resistance of the catalyst under commercial operating conditions.

Naturally occurring clays which can be composited with the catalyst include the montmorillonite and kaolin families which include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, catalysts can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary materials such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, silica-magnesia-zirconia. The matrix can be in the form of a cogel. A mixture of these components can also be used.

In general, the relative proportions of finely divided, crystalline molecular sieve component and inorganic oxide gel matrix vary widely, with the molecular sieve content ranging from about 1 to about 90 percent by weight, and more usually from about 2 to about 80 weight percent of the composite.

When the MCM-58 is mixed with another zeolite molecular sieve or when the MCM-58 is used as an additive to large-pore molecular sieve cracking catalyst inventory, the other molecular sieve or the large-pore molecular sieve component may comprise from about 5 to about 60 weight percent of the overall catalyst composition. The additive catalyst component may comprise from about 0.5 to about 50, for example, from about 2 to about 50, weight percent of the catalyst composition. For the additive catalyst, the



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crystals having the structure of MCM-58 may comprise from at least about 15 to less than about 60 weight percent of the additive catalyst component composition.

Although neither the cracking catalyst nor the additive catalyst need be steamed prior to use in the present process, they may be steamed at a temperature of from about 300°C to about 800°C for a time of from about 1 to about 200 hours in about 5 to about 100 % steam.

In an embodiment of the present invention, the catalyst composition may include metals useful in promoting the oxidation of carbon monoxide to carbon dioxide under catalyst regeneration conditions as described in U.S. Patents 4,072,600 and 4,350,614. Examples of this embodiment include addition to the catalyst composition for use herein trace amounts of oxidation promoter selected from the group consisting of platinum, palladium, iridium, osmium, rhodium, ruthenium, rhenium, and combination thereof. The catalyst composition may comprise, for example, from about 0.01 ppm to about 100 ppm by weight oxidation promoter, usually from about 0.01 ppm to about 50 ppm by weight, preferably from about 0.01 ppm to about 5 ppm by weight.

In order to more fully illustrate the nature of the invention and the manner of practicing same, the following examples are presented.

When Alpha Value is examined, it is noted that the Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and it gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). It is based on the activity of silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant =  $0.016 \text{ sec}^{-1}$ ). The Alpha Test is described in U.S. Patent 3,354,078; in the Journal of Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980). The experimental conditions of the test used herein include a constant

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temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, 61, 395.

#### EXAMPLES 1-4

5 Experiments were conducted for synthesis of crystalline product material. In these experiments,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and KOH pellets were dissolved in deionized water. The benzylquinuclidinium bromide prepared as above was then dissolved in the solutions for Examples 1, 2, and  
10 3. Benzyltropanium bromide prepared as above was dissolved in the solution for Example 4. Colloidal silica sol (30 wt.%  $\text{SiO}_2$ ) was then mixed into the solutions. The mixtures were stirred for 2 minutes to produce uniform, fluid hydrogels having compositions  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ ,  $\text{H}_2\text{O}/\text{SiO}_2 = 40$ ,  
15  $\text{OH}^-/\text{SiO}_2 = 0.30$ ,  $\text{K}^+/\text{SiO}_2 = 0.57$ , and  $\text{R}/\text{SiO}_2 = 0.20$ , where R is the cation of benzylquinuclidinium bromide or benzyltropanium bromide (Example 4).

The hydrogels of each experiment were then transferred to a 300 ml stainless steel autoclave equipped with a  
20 stirrer. The autoclave was capped and sealed; and 2758 kPa (400 psig) of inert gas was introduced into the autoclave. Stirring and heating were started immediately. Crystallizations were carried out at 170°C with stirring (2 days for Example 1 and 7 days for Examples 2-4).

25 Crystalline products were recovered, filtered, washed with deionized water, and dried on a filter funnel in an air stream under an infrared lamp. The dried crystalline powder products were proven to be MCM-58 by X-ray diffraction.

30

#### EXAMPLES 5-8

MCM-58 products of Examples 1, 2, 3, and 4 were weighed into quartz boats, then placed into a Heviduty® tube furnace and sealed with nitrogen gas flowing through  
35 the furnace tube. The heating of the furnace was begun at 2°C/minute from room temperature to 538°C. When the furnace reached the maximum temperature, the flowing gas

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was switched to air, and the calcination of the zeolite was continued for 15 hours before termination.

5 The air calcined samples were ammonium exchanged with 1 M  $\text{NH}_4\text{NO}_3$  at  $80^\circ\text{C}$  for 6 hours. After ammonium exchange, the zeolites were filtered, washed with deionized water, and dried in an air stream on the filter funnel under an infrared heat lamp.

10 The calcination procedure was repeated on the ammonium-exchanged materials in the tube furnace in the same manner as described above, except this time the samples were held at  $538^\circ\text{C}$  for 8 hours to convert them to HMC-58. Examples 5, 6, 7, and 8 products were MCM-58 materials from the products of Examples 1, 2, 3, and 4, respectively.

15

#### EXAMPLE 9

20 Samples of the HMC-58 products of Examples 5, 6, and 7 were tested for catalytic cracking activity in the Alpha Test and found to have Alpha Values of 521, 164, and 510, respectively.

#### Constraint Index

25 A convenient measure of the extent to which a crystalline material provides control to molecules of varying sizes to its internal structure is the Constraint Index (CI) of the material. Zeolites which provide a highly restricted access to and egress from their internal structures have a high value for the Constraint Index, and zeolites of this kind usually have pores of small size, e.g., less than 5 Angstroms. On the other hand, zeolites which provide relatively free access to their internal structures have a low value for the Constraint Index and usually have pores of large size, e.g., greater than 8 Angstroms. The method by which Constraint Index is  
35 determined is described fully in U.S. Patent No. 4,016,218.

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EXAMPLE 10

The Constraint Index of the HMC-58 product of Example 6 was determined to be 0.3 at 316°C. This value falls within the classification of the more open structures having 12-membered rings. Hence, it is concluded from the catalytic Constraint Index Test result that HMC-58 contains at least a 12-membered ring structure.

EXAMPLE 11

Catalyst "A" containing 40% HMC-58, prepared as in Example 6, in a silica-alumina-clay matrix was produced by spray drying according to the following procedure.

Thirty grams of alumina (Condea) were slurried in distilled water and peptized with formic acid. The resulting gel was added to 596 grams of colloidal silica (Nalco 1034A) and mixed for 3 minutes. A 300 gram quantity of ball milled HMC-58 was added to the silica-alumina slurry. A 372 gram quantity of Kaolin clay (Thiele RC-30) was added to the slurry while maintaining the pH between 3 and 4. The slurry was spray dried with an outlet temperature of 177°C (350°F). The spray-dried product was then calcined for 2 hours at 538°C (1000°F).

The resulting Catalyst A comprised 40% HMC-58 and 60% matrix (45.5% silica, 4.5% alumina, and 50% clay).

EXAMPLE 12

Catalyst A was tested using a Fixed Fluid Bed (FFB) reactor with sour heavy gas oil having the properties of Table II with catalyst to oil ratio of 3. Reaction conditions included a temperature of 515°C (960°F), a pressure of 29.66 inches of Hg, and 1 minute time on stream. The results of this test presented in Table III show that MCM-58 is an active catalyst for the present process.

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TABLE II

	API Gravity, 60°F (15°C)	20.1
	Pour Point	95
5	KV @ 40°C, cs	104.8
	KV @ 100°C, cs	7.95
	Aniline Point	168.5
	Bromine Number	6.9
	CCR, wt.%	0.56
10	Sulfur, wt.%	2.6
	Carbon, wt.%	85.1
	Hydrogen, wt.%	12.3
	Nitrogen, wt.%	0.16
	Basic Nitrogen, ppm	465
15	Nickel, ppm	0.48
	Vanadium, ppm	0.29
	Iron, ppm	1.2
	Copper, ppm	0.01
	Na, ppm	0.8
20	Paraffins, wt.%	17.9
	Mono Naphthenes, wt.%	13.5
	Poly Naphthenes, wt.%	13.3
	Aromatics	55.3
25	<u>Distillation</u>	
	<u>Boiling Range</u>	<u>°F</u>
	IBP	497
	5 vol.%	633
30	10 vol.%	677
	20 vol.%	726
	30 vol.%	760
	40 vol.%	792
	50 vol.%	826
35	60 vol.%	859
	70 vol.%	899
	80 vol.%	945
	90 vol.%	1001
40	EP	1024

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TABLE III

	Cat/oil	3
	Conversion, % vol.	66
5	C <sub>5</sub> <sup>+</sup> gasoline, % vol.	31
	Alkylate, % vol.	29
	C <sub>3</sub> =, % vol.	12
	C <sub>4</sub> =, % vol.	5
	Gasoline + alkylate, % vol.	60
10	Light gas, % wt.	3.0
	Coke, % wt.	8
	LFO, % wt.	22
	HFO, % wt.	15

15

EXAMPLE 13

Catalyst "B" was prepared by steaming Catalyst A at 649°C (1200°F) for 4 hours using 45% steam and 55% air. Table IV shows the results of our FFB test on this catalyst which shows improved selectivity as the acid site density decreases. Coke has dropped and gasoline plus alkylate product increased slightly even at lower conversion.

20

TABLE IV

25	Cat/oil	3
	Conversion, % vol.	57
	C <sub>5</sub> <sup>+</sup> gasoline, % vol.	32
	Alkylate, % vol.	29
	Gasoline + alkylate, % vol.	61
30	Coke, % wt.	4
	LFO, % wt.	24
	HFO, % wt.	23

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EXAMPLE 14

Catalyst "C" was prepared by steaming Catalyst B at 760°C (1400°F) for 4 hours using 45% steam and 55% air.

5 Table V shows the results of our FFB test on this catalyst and compares it with a 40% USY catalyst in a similar matrix and steamed for 10 hours at 1450°F in 45% steam.

TABLE V  
Catalyst C                      USY

10	Conversion, % vol.	65%	65%
	C <sub>5</sub> <sup>+</sup> gasoline, % vol.	36.8	53.6
	C <sub>3</sub> =, % vol.	13.1	5.7
15	C <sub>4</sub> =, % vol.	9.9	6.0
	Alkylate, % vol.	38.2	19.6
	Gasoline + alkylate, % vol.	75.0	73.3
20	Coke, % wt.	5.1	4.7
	LFO, % wt.	22.7	28.9
	HFO, % wt.	15.5	8.5
	RON, raw gasoline	95.2	89.0

25 The results in Table V show that MCM-58 has good stability after steaming at 760°C (1400°F). Furthermore, the differences between MCM-58 and USY are observed. MCM-58 makes significantly more light olefins, i.e., C<sub>3</sub><sup>-</sup> and C<sub>4</sub><sup>-</sup>, that, if added to the gasoline, produce a greater amount of

30 gasoline + alkylate. The octane (RON) for the raw gasoline from MCM-58 catalyst is also much greater than that from USY catalyst. This Example shows that MCM-58 is an excellent octane catalyst with good yields for gasoline + alkylate, and high yields of lower molecular weight

35 olefins.

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EXAMPLE 15

Catalyst "D" was prepared by steaming Catalyst C at 788° (1450°F) for 4 hours using 45% steam and 55% air.

Table VI shows the results of our FFB test on this catalyst. This Example shows that MCM-58 has good steam stability.

TABLE VI

	Cat/oil	5.8
10	Conversion, % vol.	57.8
	C <sub>5</sub> <sup>+</sup> gasoline, % vol.	38.5
	Alkylate, % vol.	26.7
	Gasoline + alkylate, % vol.	65.2
	Outside iC <sub>4</sub> for alkylate, % vol.	10.8
15	Coke, % wt.	4.31
	RON, raw gasoline	94.7
	RON, C <sub>5</sub> <sup>+</sup> gasoline	94.4
	RON, C <sub>5</sub> <sup>+</sup> gasoline + alkylate	94.2

20

The gasoline produced during this experiment was submitted for gas chromatographic analysis of gasoline range materials. Table VII shows the composition of the gasoline and compares it with that of a commercial REUSY equilibrium catalyst having the following properties:

	Silica, wt.%	54.2
	Alumina, wt.%	34.4
	Ash, wt.%	99.58
30	Rare Earth, wt.%	3.0
	Sodium, wt.%	0.32
	Surface Area, m <sup>2</sup> /g	124
	Bulk Density, (Loose) g/cc	0.85
	Bulk Density, (Packed), g/cc	0.96
35	Particle Density, g/cc	1.385
	Real Density, g/cc	2.648
	Pore Volume, cc/g	0.34
	Pore Diameter, A	110

40



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TABLE VII

	<u>Catalyst D</u>	<u>REUSY Catalyst</u>
	58	59
Hydrocarbon conv., % vol.		
5 <u>Gasoline composition</u>		
Naphthenes, % wt.	8.3	10.9
Iso-paraffins, % wt.	13.5	22.5
N-paraffins, % wt.	2.3	1.7
Cyclic-olefins, % wt.	13.3	6.6
10 Iso-olefins, % wt.	18.1	13.2
N-olefins, % wt.	6.5	6.9
Aromatics, % wt.	36.0	32.0
>390 °F HC, % wt.	2.1	6.3
15 C <sub>5</sub> <sup>+</sup> gasoline octane	94.4	90.1

EXAMPLE 16

Catalyst "E", made from a mixture of 5% catalyst A with 95% of the commercial REUSY equilibrium catalyst, was used to test MCM-58 as an additive. The results presented in Table VIII show the effect of MCM-58 as an additive catalyst and demonstrate its effectiveness as an octane and gasoline plus alkylate enhancement additive when compared with results obtained for the commercial REUSY catalyst.

25

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TABLE VIII

		<u>Catalyst E</u>	<u>REUSY Catalyst</u>
	Cat/oil	3	3
5	Conversion, % vol.	64.5	61.2
	C <sub>5</sub> <sup>+</sup> gasoline, % vol.	47.0	50.2
	Light gas, % wt.	2.0	2.7
	Total C <sub>3</sub> , % vol.	13.2	8.9
	Total C <sub>4</sub> , % vol.	15.7	11.1
10	Coke, % wt.	3.56	3.37
	LFO, % wt.	27.1	29.1
	HFO, % wt.	11.3	11.9
	Gasoline + distillate, % wt.	66.0	70.1
15	Alkylate, % vol.	28.4	20.6
	Gasoline + alkylate, % vol.	75.4	70.8
20	Outside iC <sub>4</sub> for alkylate, % vol.	11.5	9.8
	RON, raw gasoline	93.8	90.2
25	RON, C <sub>5</sub> <sup>+</sup> gasoline	93.3	89.9
	RON, C <sub>5</sub> <sup>+</sup> gasoline + alkylate	93.5	91.0

30

EXAMPLE 17

Catalyst "F", a mixture of 25% catalyst D and 75% REUSY equilibrium catalyst, was tested in our FFB unit. Table IX shows that MCM-58 can be used effectively to

35

increase the octane of gasoline range products.

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TABLE IX

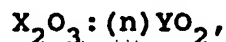
Catalyst FREUSY Catalyst

5	Crackability	2.3	2.3
	Conversion, % vol.	70.0	70.0
	C <sub>5</sub> <sup>+</sup> gasoline, % vol.	55.0	56.4
10	Light gas, % wt.	2.2	2.3
	Total C <sub>3</sub> , % vol.	10.6	9.9
	Total C <sub>4</sub> , % vol.	13.3	12.3
15	Coke, % wt.	4.97	4.75
	LFO, % wt.	26.2	26.2
	HFO, % wt.	7.1	7.0
20	Gasoline + distillate, % wt.	71.6	72.9
	Alkylate, % vol.	22.5	20.8
	Gasoline + alkylate, % vol.	77.5	77.2
25	Outside iC <sub>4</sub> for alkylate, % vol.	8.9	8.3
	RON, raw gasoline	91.9	90.7
30	RON, C <sub>5</sub> <sup>+</sup> gasoline	91.5	90.4
	RON, C <sub>5</sub> <sup>+</sup> gasoline + alkylate	92.1	91.3

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What is Claimed is:

1. A process for converting feedstock hydrocarbon compounds to product hydrocarbon compounds having a lower molecular weight than the feedstock hydrocarbon compounds which comprises contacting said feedstock at conversion conditions with a catalyst composition comprising an active form of synthetic porous crystalline material characterized by an X-ray diffraction pattern including values as set forth in Table I of the specification and having a composition comprising the molar relationship



wherein n is from greater than 10 to 1000, X is a trivalent element, and Y is a tetravalent element.

2. The process of claim 1 wherein n is from greater than 10 to 400.

3. The process of claim 1 wherein n is from 20 to 200.

20

4. The process of claim 1, 2 or 3 wherein said crystalline material comprises cations selected from the group consisting of hydrogen, hydrogen precursors, rare earth metals, metals of Groups IIA, IIIA, IVA, IB, IIB, IIIB, IVB, VIB and VIII of the Periodic Table of the Elements, and combinations thereof.

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5. The process of claim 1, 2, 3 or 4 wherein X is trivalent boron, iron, indium, gallium, aluminum, or a combination thereof; and Y is tetravalent silicon, tin, germanium, or a combination thereof.

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6. The process of claim 5 wherein X comprises aluminum, boron, or a combination thereof and Y comprises silicon.

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7. The process of claim 1 wherein said catalyst composition comprises a matrix of alumina, silica, zirconia, titania, magnesia, beryllia, clay, or a combination thereof.

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8. The process of claim 1 wherein said catalyst composition comprises phosphorus.

9. The process of claim 1 wherein said conversion conditions include temperature of from 400°C to 650°C and a pressure of from atmospheric to 5 atmospheres.

10. The process of claim 1 wherein said conversion conditions include an average reactor temperature of from 450°C to 540°C, a catalyst/oil volume ratio of from 2 to 7, and a volume hourly space velocity of from 1 to 5 hr<sup>-1</sup>.

11. The process of claim 1 wherein said conversion conditions include a riser top temperature of from 500°C to 595°C, a catalyst/oil weight ratio of from 3 to 12, and a catalyst residence time of from 0.5 to 15 seconds.

12. The process of claim 1, 4, 7 or 8 wherein said catalyst composition further comprises another molecular sieve component of large-pore crystalline material having pore openings of greater than 7 Angstroms diameter, intermediate-pore crystalline material having pore openings of from 4 Angstroms to 7 Angstroms diameter, small-pore crystalline material having pore openings of less than 4 Angstroms diameter, or combinations thereof.

13. The process of claim 1, 4, 7 or 8 wherein said catalyst composition further comprises another molecular sieve component having the structure of ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57 or SAPO-31.

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14. The process of claim 1, 4, 7 or 8 wherein said catalyst composition further comprises a large-pore molecular sieve component of zeolites X, REX, Y, USY, REY, REUSY, DeAlY, UHPY, LZ-210, Beta, ZSM-20, L, silicoaluminophosphates SAPO-5, SAPO-37, SAPO-40, MCM-9, pillared silicates, pillared clays or mesoporous crystalline MCM-41.

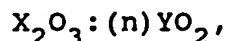
15. The process of claim 14 wherein the large-pore molecular sieve component comprises Y, REY, USY, or REUSY.

16. The process of claim 1, 4, 7, 8 or 12 wherein said feedstock comprises a gas oil having an initial boiling point above 204°C and an end point of at least 315°C.

17. The process of claim 1, 4, 7, 8 or 12 wherein said feedstock comprises deep cut gas oil, vacuum gas oil, thermal oil, residual oil, cycle stock, whole top crude, tar sand oil, shale oil, or a product of hydrotreatment thereof.

18. The process of claim 1, 4, 7, 8 or 12 wherein said catalyst composition further comprises from 0.01 ppm to 100 ppm by weight of platinum, palladium, iridium, osmium, rhodium, ruthenium or rhenium.

19. A process for cracking feedstock hydrocarbon compounds to product comprising gasoline which comprises contacting said feedstock at cracking conditions including a temperature of from 400°C to 650°C with a catalyst composition comprising an active form of synthetic porous crystalline material characterized by an X-ray diffraction pattern including values as set forth in Table I of the specification and having a composition comprising the molar relationship



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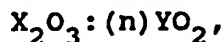
wherein n is from greater than 10 to 1000, X is a trivalent element, and Y is a tetravalent element.

20. The process of claim 19 wherein said catalyst  
5 composition further comprises the large-pore molecular sieve material of zeolites Y, REY, USY, and REUSY.

21. The process of claim 19 wherein said catalyst  
10 composition further comprises another molecular sieve component having the structure of ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57 or SAPO-31.

22. The process of claim 19, 20 or 21 wherein said  
15 catalyst composition further comprises from 0.01 ppm to 100 ppm by weight of platinum, palladium, iridium, osmium, rhodium, ruthenium or rhenium.

23. A process for converting feedstock hydrocarbon  
20 compounds to product comprising propylene or butylene which comprises contacting said feedstock at conversion conditions with a catalyst composition comprising an active form of synthetic porous crystalline material characterized by an X-ray diffraction pattern including values as set  
25 forth in Table I of the specification and having a composition comprising the molar relationship



wherein n is from greater than about 10 to about 1000, X is a trivalent element, and Y is a tetravalent element.

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24. The process of Claim 23 wherein said catalyst composition further comprises another molecular sieve component structure of ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57 or SAPO-31.

25. The process of Claim 23 wherein said catalyst composition further comprises a large-pore molecular sieve component of zeolites X, REX, Y, USY, REY, REUSY, DeAlY, UHPY, LZ-210, Beta, ZSM-20, L, silicoaluminophosphates SAPO-5, SAPO-37, SAPO-40, MCM-9, pillared silicates, pillared clays or mesoporous crystalline MCM-41.



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/05253

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10G 11/04, 11/05; C07C 4/06

US CL :208/113, 114, 118, 119, 120; 585/653

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/113, 114, 118, 119, 120; 585/653

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, STN (apipat, apilit, ca) - search terms: MCM-58

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 5,437,855 (VALYOCSIK) 01 August 1995.	1-4, 7-11, 19-25
A,P	US, A, 5,441,721 (VALYOCSIK) 15 August 1995.	1-4, 7-11, 19-25
A	US, A, 5,126,298 (ABSIL ET AL.) 30 June 1992.	1-4, 7-11, 19-25
A	US, A, 5,110,776 (CHITNIS ET AL.) 05 May 1992.	1-4, 7-11, 19-25
A	US, A, 4,927,523 (DONNELLY) 22 May 1990.	1-4, 7-11, 19-25
A	US, A, 4,309,280 (ROSINSKI ET AL.) 05 January 1982.	1-4, 7-11, 19-25

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

10 JUNE 1996

Date of mailing of the international search report

24 JUL 1996

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/05253

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,758,403 (ROSINSKI ET AL.) 11 September 1973.	1-4, 7-11, 19-25

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/05253

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5, 6, AND 12-18  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.